

Chapter 4

Synthesis of Nanomaterials—II

(Chemical Methods)

4.1 Introduction

In this chapter we shall discuss some of the wet chemical methods to synthesize nanomaterials. There are numerous advantages of using chemical methods which are summarized in Box 4.1. In some cases nanomaterials are obtained as colloidal particles in solutions, which can be filtered and dried to obtain powder. We can obtain thin films or nanoporous materials by electrodeposition and etching. Advantages of chemical synthesis are manifold. In many cases very well known chemical reaction route can be optimized to obtain nanoparticles. Particles of different shapes and sizes are possible depending upon the chemicals used and reaction conditions.

Box 4.1: Some Advantages of Chemical Synthesis

- Simple techniques
- Inexpensive, less instrumentation compared to many physical methods
- Low temperature (<350 °C) synthesis
- Doping of foreign atoms (ions) possible during synthesis
- Large quantities of the materials can be obtained
- Variety of sizes and shapes are possible
- Materials are obtained in the form of liquid but can be easily converted into dry powder or thin films
- Self assembly or patterning is possible

Low to high temperature routes are possible. In many cases, particles can be doped with different metal ions quite easily. Coupled, coated, chemically capped (by some molecules or passivated) particles can be made. Most important is that very narrow size distributed materials are possible to synthesize and in many cases

large quantities of materials can be obtained. The instrumentation involved in the chemical synthesis can be relatively simple and inexpensive as compared to many physical methods. As in many cases nanoparticles synthesized by chemical method form what is known as ‘colloids’. We shall first try to understand them and then proceed to some specific chemical routes to obtain them as nanoparticles.

4.2 Colloids and Colloids in Solutions

Colloids are known since very long time. A class of materials, in which two or more phases (solid, liquid or gas) of same or different materials co-exist with the dimensions of at least one of the phases less than a micrometre is known as colloids. Colloids may be particles, plates or fibres (see Fig. 4.1). Nanomaterials are a subclass of colloids, in which one of the dimensions of colloids is in nanometre range.

There are several examples around us, having different combinations of phases, in the form of colloids like liquid in gas (fog), liquid in liquid (fat droplets in milk), solid in liquid (tooth paste), solid in solid (tinted glass), gas in liquid (foam). There can be multiple existing colloids like water and oil bubbles in porous mineral rocks. Organic and inorganic materials can be dispersed into each other to form colloids. Several examples exist even of bio-colloids. Blood and bones are good examples of bio-colloids. Blood has corpuscles dispersed in serum and bone has colloids of calcium phosphate embedded in collagen.

Colloids may even form networks. For example aerogels (discussed in more details in Chap. 9) are a network of silica colloidal particles, pores of which are filled with air.

4.2.1 Interactions of Colloids and Medium

Colloids are particles with large surface to volume ratio. Correspondingly there are large number of atoms/molecules on the surface of a colloidal particle, which

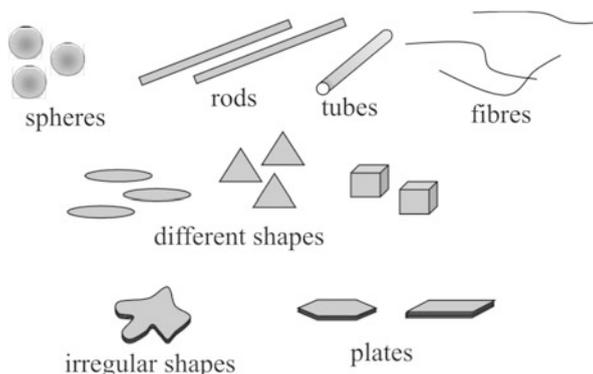


Fig. 4.1 Different shapes of colloids

do not have as many neighbours as those for an atom/molecule inside the interior. Therefore atoms on the surface are in a highly reactive state, which easily interact to form bigger particles or tend to coagulate. It is thus necessary to understand the stability of colloids i.e. how the colloids dispersed in a medium can remain as separated particles. In general there are a number of interactions involved. For the sake of understanding these interactions, we consider the inorganic spherical colloids of equal size, dispersed in a liquid medium. When fine particles are dispersed in a liquid medium, it is known that they undergo *Brownian motion* (Box 4.2). If we are able to tag a particle in the solution, as depicted in Fig. 4.2, it would appear as if it is making a random motion. All other particles also execute random motion, hitting each other and changing direction of motion in solution. Distance travelled between successive collisions is random too. However an average distance travelled by a colloidal particle can be found as

$$\Delta \bar{R}^2 = \left(\frac{kT}{3\pi r \eta} \right) \Delta t \quad (4.1)$$

where $\Delta \bar{R}$ is distance travelled by a particle from its original position in time Δt , k – Boltzmann's constant, T – temperature of liquid, r – particle radius and η is viscosity of the liquid.

Box 4.2: Robert Brown (1773–1858)

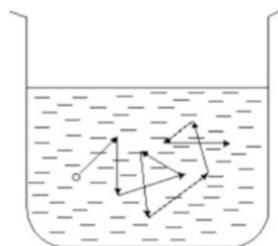
Robert Brown who discovered Brownian motion in 1827 was born on 21st December 1773 in Montrose, Scotland. He studied medicine at the University of Edinburgh. Immediately after completing his education he joined Fifeshire Regiment of Fencibles as Ensign and Surgeon's Mate. In his free time he used to study botany. On 18th July 1801 he joined an eminent botanist Sir Joseph Banks to go to Australia on an expedition. Their goal was to collect some rare plants and study them. They returned back to England in October 1805 with a huge collection of some 4,000 species of plants, some zoological specimens and numerous drawings and notes. Brown spent next five years working on this material. Brown used a microscope throughout his studies. He is considered to be a 'gifted observer'. He identified naked ovule in the gymnosperm which is a rather difficult task even using modern microscopes. He however is famous due to 'Brownian motion' which he observed in pollen grains using his simple optical microscope. Others also had observed such motion of particles under microscope but they simply attributed it to 'life' itself. Careful experiments by Brown showed that they were not the consequence of 'life' nor any currents in fluids or evaporation of liquid.

(continued)

Box 4.2 (continued)

From 1806 to 1822 Robert Brown served as a clerk, librarian and housekeeper of the Linnen Society of London. He was elected as fellow of Royal Society in 1810 and fellow of Linnen Society in 1822. He remained the president of Linnen Society from 1849 to 1853. He died on 10th June 1858 in London.

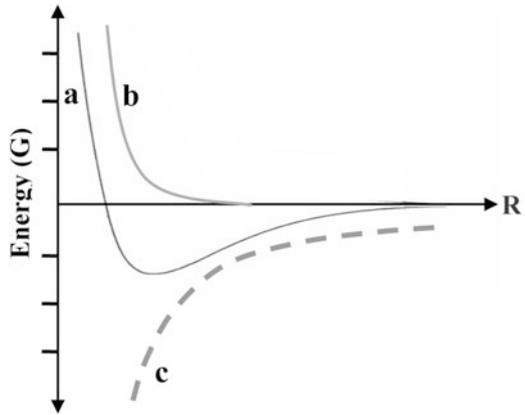
Fig. 4.2 Brownian motion of colloidal particles



Interactions of such constantly and randomly moving particles with each other and with liquid in general would be quite complex. Consider for example the van der Waals interaction (see Chap. 2) between two atoms or molecules. There are two parts in the interaction viz. attractive and repulsive parts given by the Eq. (4.2), irrespective of whether there exist permanent dipoles or not. The interaction is given as

$$dG_1 = \left(\frac{A}{R^{12}} \right) - \left(\frac{B}{R^6} \right) \quad (4.2)$$

Fig. 4.3 Van der Waals interaction: (a) Resulting energy, (b) Repulsive energy and (c) Attractive energy



where dG_I is the interaction energy, A and B are constants and R is the distance between two particles.

Here the first term is repulsive interaction (Born repulsive interaction) effective only at short distance and second term represents long range attractive interaction (van der Waals attraction). Repulsive part arises due to repulsion between electron clouds in each atom and attractive part is due to interaction between fluctuating or permanent dipoles of atoms/molecules. Schematically it is shown in Fig. 4.3. Equation (4.2) is known as Lennard-Jones equation (Box 4.3).

Box 4.3: Free Energy

Free energy of a body is a measure of its ability to do work. A body always tends to attain the state of lower energy by releasing ‘free energy’ and is given by Gibb’s free energy

$$G = H - TS \tag{4.3}$$

where G is the energy absorbed or released by a body, H – enthalpy, T – temperature and S is entropy.

In order to understand the meaning of surface free energy, consider that a cylinder with cross section ‘ A ’ and length ‘ $2l$ ’ is cut into two equal pieces as shown in Fig. 4.4. Work has to be done in order to break the cylinder into two pieces and separate them by a distance R .

Energy increases as the distance between the two pieces increases. The two pieces keep on attracting each other due to intermolecular forces at the broken interface. Therefore, more and more energy has to be supplied in order to separate them. Interfacial energy is related to the surface tension ‘ γ ’.

(continued)

Box 4.3 (continued)

Fig. 4.4 A cylinder with cross section A and length $2l$ has been cut into two pieces of equal length

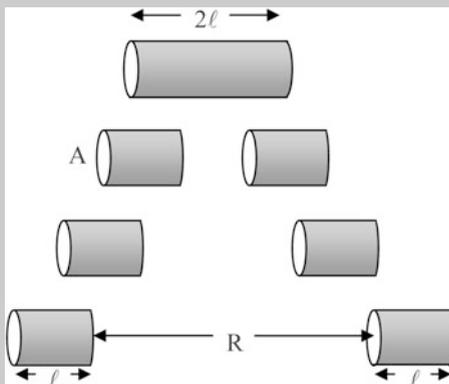
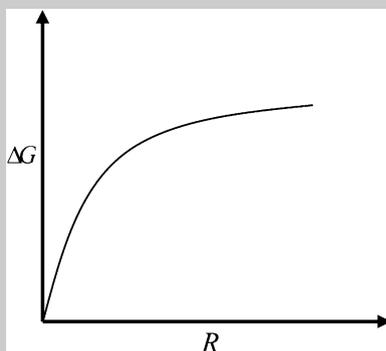


Fig. 4.5 Change in surface free energy with separation R between two pieces of the cylinder shown in Fig. 4.4



Surface tension γ is along the normal to surface and is expressed as force per unit length (N/m or Joule/m²). Surface free energy is given by

$$\Delta W = \Delta G - 2\gamma A \quad (4.4)$$

where ΔW is the work done to break the cylinder, γ —surface tension and A is the surface area. (Factor ‘2’ arises because while creating two surfaces, surface area would be $2A$ for two surfaces as shown in Fig. 4.4).

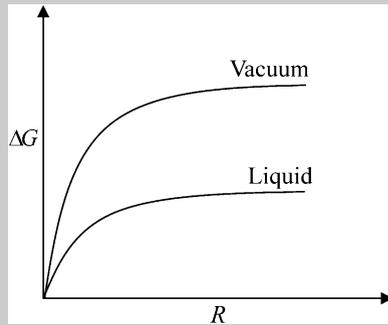
The surface free energy per unit volume would increase as shown in Fig. 4.5 with separation R between two particles.

The force of attraction would increase in vacuum as shown in Fig. 4.6. In a liquid the force of attraction would reduce in general.

(continued)

Box 4.3 (continued)

Fig. 4.6 Change in surface free energy with separation R between two pieces of the cylinder shown in Fig. 4.4, placed in vacuum or liquid



4.2.2 Colloids in Vacuum

Lennard-Jones equation (4.2) is sufficient to describe an interaction between two atoms or molecules. When we consider colloids with large number of atoms, we need to take into account all the atoms and their interactions with each other. This is quite a complex situation as shown in Fig. 4.7. To describe the interaction between colloidal particles Derjaguin, Landau, Verwey and Overbeek proposed a theory known as DLVO theory. In order to reduce the complexity of the problem, they assumed two interacting spherical particles of equal size. Let the radius of each particle be ' r ' and let two particles be separated by a distance ' R '.

It was shown that for two similar spherical particles in vacuum the attractive interaction is given by

$$dG \text{ (attraction)} = - \left(\frac{A_H \cdot r}{12R} \right) \left[1 + \frac{3}{4} \cdot \frac{R}{r} \right] \tag{4.5}$$

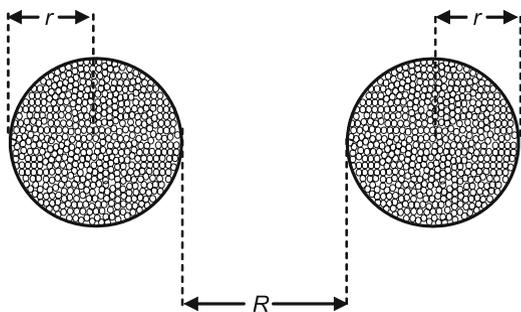


Fig. 4.7 Interaction even between two spherical particles of same material and same size is complex due to presence of large number of atoms in each particle

where A_H is known as Hamaker constant and is given by

$$A_H = A' \pi^2 n^2 \quad (4.6)$$

where A' is a constant related to A in the Lennard-Jones equation (4.2) and n is the number of atoms/molecules per unit volume in a colloid.

4.2.3 Colloids in a Medium

So far we considered the colloids just in vacuum. Consider now a situation, in which inorganic spherical colloids are immersed in a liquid (and do not dissolve). The attractive interactions between the colloids get modified through the change of Hamaker constant as A_H , which can be written now as

$$A_H = \left(\sqrt{A_{1v}} - \sqrt{A_{2v}} \right)^2 \quad (4.7)$$

where A_{1v} is the Hamaker constant for particle of inorganic solid under consideration, in vacuum and A_{2v} is Hamaker constant of colloid of medium in vacuum. It can be seen from above equation that in general the effect of liquid medium is to reduce the Hamaker constant of colloid particle. Hence the attractive force between colloid particles will in general reduce.

4.2.4 Effect of Charges on Colloids

Colloids in liquid may be positively charged, negatively charged or even neutral. But in most of the cases they are charged. There are various sources for colloids by which they acquire charges on their surfaces viz. through composition of colloidal material, properties of dispersing medium including the type and concentration of dissolved ions in the solution. In any case as soon as there are some charges on particles, ions of opposite charges accumulate around them. Oppositely charged ions are known as *counter ions*.

This accumulation of counter ions leads to formation of an electric double layer. Helmholtz considered that the situation is like that in a parallel plate condenser, where there are opposite charges as plates separated by a medium (for example air as shown in Fig. 4.8). Due to their Brownian motion, counter ions are not fixed nor are colloidal particles at rest. They execute their own Brownian motion and form a dynamic double layer around them as schematically shown in Fig. 4.9.

The changes occur when concentrations of charges on colloid and local ionic charges in solution contribute to double layer change. The concentration of electrolyte would strongly affect the electric potential curve and is shown schematically in Fig. 4.10.

Fig. 4.8 Double layer of charges and fall of electrical potential from negatively charged plate with positive ion accumulation

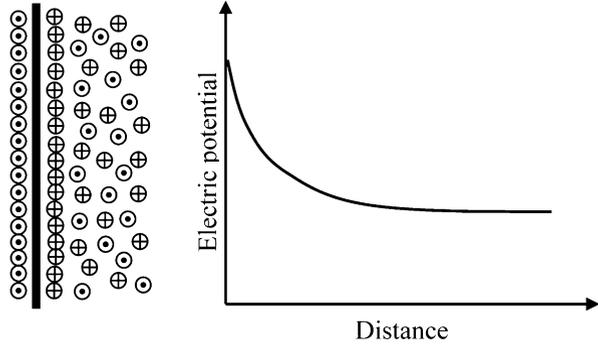


Fig. 4.9 Diffuse double layer because of Brownian motion

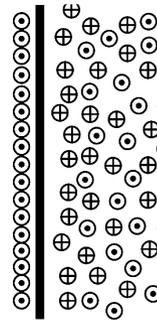
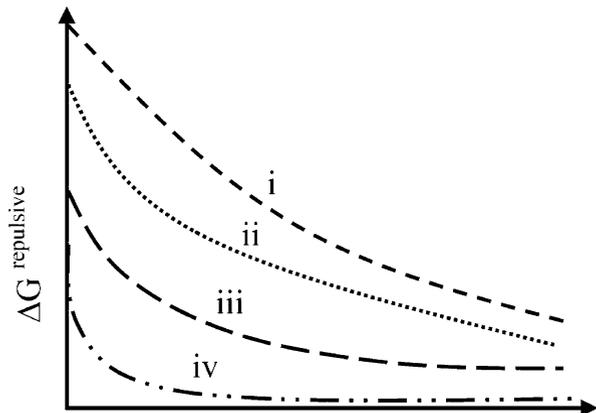


Fig. 4.10 Effect of concentration on change of potential from a particle. Curves *i, ii, iii* and *iv* refer to increasing electrolyte concentrations



Consider now a situation in which two charged colloidal particles come closer with their electric double charge layers. As they approach each other force of repulsion increases as shown in Fig. 4.11. It is easy to see that the difference in concentrations of double layer charges would play an important role.

The repulsive interaction for low concentration would set at longer distance and that for higher concentration at smaller distance.

Fig. 4.11 Colloid-colloid interaction with electric double charge layer

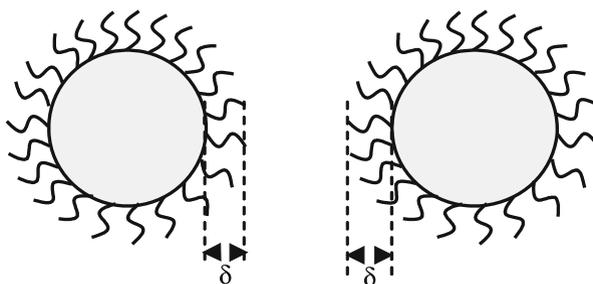
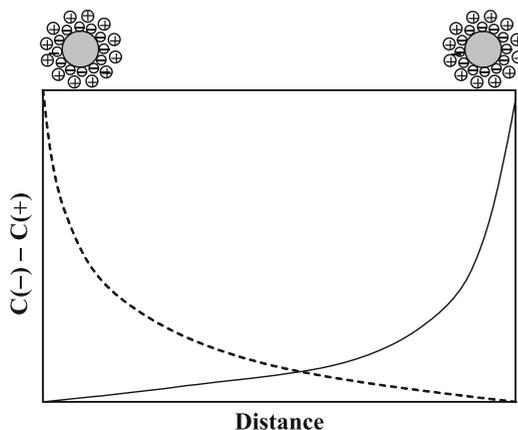


Fig. 4.12 Colloids with coatings. Separation between the particles, each coated with coating of thickness δ , increases by 2δ

4.2.5 Stearic Repulsion

Stability of colloids can be increased by creating Stearic hindrance or repulsion (see Fig. 4.12).

By adsorbing some layers of a different material on colloidal particles e.g. polymer or organic molecules on inorganic colloidal particles, it is possible to reduce the attractive forces between them. With addition of adsorbed layers, the effective sizes of the particles change which helps them to stay at a longer distance from each other, reducing the attractive interaction. However, in case where the coating material is similar in properties to that of the solvent, the effect of coating would be negligible. By anchoring long chain molecules on the particles, it is possible to keep them apart with negligible interaction. This idea is the basis of 'capped nanoparticles' discussed in the next section.

Thus the colloids interact with each other dynamically and are affected by van der Waals forces, colloid-colloid interaction mediated through dispersing medium, electric double layer and Stearic interactions. All the interactions may not be set in for every case. In general, contributions of these various attractive and repulsive

interactions—also dictated by temperature, concentration of colloids and dispersing medium—are additive and can be written as follows.

$$\begin{aligned}\Delta G = & \Delta G_1 \text{ (attractive and repulsive)} + \Delta G_2 \text{ (colloid-colloid attractive)} \\ & + \Delta G_3 \text{ (electrostatic repulsion)} + \Delta G_4 \text{ (Stearic repulsion)} \\ & + \Delta G_5 \text{ (any other)}\end{aligned}\quad (4.8)$$

If the repulsive forces are strong enough, colloids would be stabilized. Otherwise ripening, coagulation, or network formation may take place.

4.2.6 *Synthesis of Colloids*

Colloids are thus phase separated submicrometre particles in the form of spherical particles or particles of various shapes and sizes like rods, tubes, plates. They are the particles suspended in some host matrix. Metal, alloy, semiconductor and insulator particles of different shapes and sizes can be synthesized in aqueous or non-aqueous media. Colloidal particles in liquids are stabilized as discussed above by Coulombic repulsion, which arises due to similar charges they may have acquired on their surfaces. In some cases surface passivating molecules may be used which provide sufficient steric hindrance inhibiting coalescence or aggregation. Nanomaterials are a special class of colloidal particles which are few hundreds of nanometre or smaller in size.

Synthesis of colloids is a very old method. Making nanoparticles using colloidal route goes back to nineteenth century when M. Faraday synthesized gold nanoparticles by wet chemical route. The particles are so stable that even today the colloidal solution made by him can be seen in the British Museum in London.

Here we shall discuss some commonly used synthesis methods of metal, semiconductor and insulator nanoparticles with some examples.

Chemical reactions in which colloidal particles are obtained are carried out in some glass reactor of suitable size. Glass reactor usually has a provision to introduce some precursors, gases as well as measure temperature and pH during the reaction. It is usually possible to remove the products at suitable time intervals. Reaction is usually carried out under inert atmosphere like argon or nitrogen gas so as to avoid any uncontrolled oxidation of the products. There is also a provision made to stir the reactants during the reaction by using teflon-coated magnetic needle. Figure 4.13 illustrates a simple chemical synthesis set up to obtain nanoparticles by colloidal route.

4.3 Nucleation and Growth of Nanoparticles

Synthesis of nanoparticles of different shapes and sizes may appear as a complex process. Over several decades, scientists have tried to understand the process of atom-by-atom nucleation and growth of small to large particles in melts, aqueous or

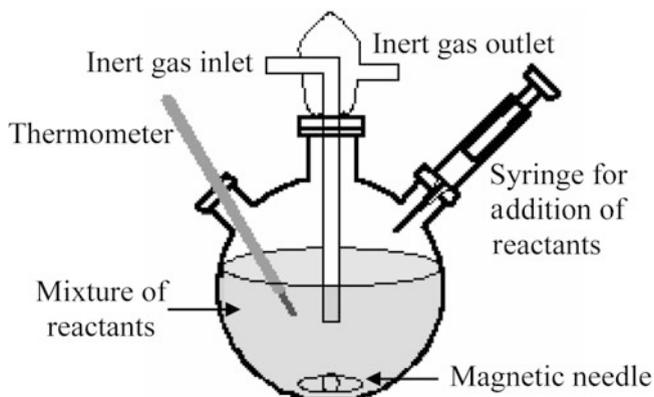


Fig. 4.13 A typical chemical reactor to synthesize nanoparticles

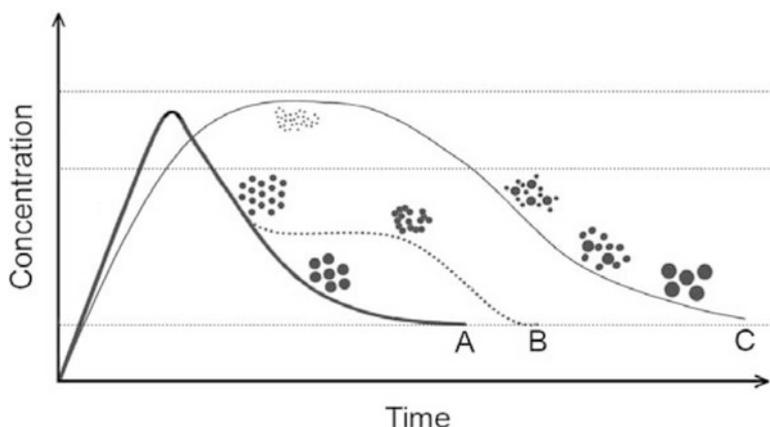


Fig. 4.14 Nucleation and growth of nanoparticles (LaMer diagram). All the dots appearing in the sketch are small/big nanoparticles

non-aqueous media from gas phase, or even in solids. The process of nucleation is a ‘bottom-up’ approach in which atoms and/or molecules come together to form a solid. The process can be spontaneous, and it may be homogenous or heterogeneous nucleation. Homogenous nucleation is said to take place when it involves the nucleation around the constituent atoms or molecules of the resultant particles. Heterogeneous nucleation, on the other hand, can take place on a foreign particle like dust, deliberately adding seed particles, templates, or the walls of the container.

Nucleation can also occur by a cavitation process. In cavitation, if there are some bubbles (which can be formed deliberately, as discussed in a later section) in the solution which then collapse, the high local temperature and pressure thus generated may be sufficient to cause homogenous nucleation. It can be seen in curve A of Fig. 4.14 that fast nucleation takes place as the solute concentration approaches

super saturation. If the nuclei acquire atoms quickly by diffusion through solution thus reducing the solute concentration, particles of uniform size are formed in a relatively shorter time compared to aggregated particles in curve B, or *Ostwald-ripened* particles as in C.

In the Ostwald ripening process, the nucleation proceeds for a long time bringing in smaller and larger nuclei to co-exist when super-saturation region exists over a longer period and then the solute concentration decreases. Larger particles tend to grow at the expense of smaller ones, thus becoming even larger. This is because of the lowering of total surface energy. It should be remembered that the concentration of solutes and temperature of the solution would strongly affect the growth. Additionally, the crystalline structure, defects, favourable sites, etc. would strongly affect the final products.

As schematically illustrated in Fig 4.14, once the nuclei are formed they may take different routes—A, B, or C—depending on the growth conditions. The growth route depicted by curve A is a classical route suggested by LaMer, and is hence called as a LaMer diagram.

Nucleation process is controlled (except in bio-minerals, to be discussed in Chap. 5) thermodynamically. The size of a nucleus is determined by both the free energy change occurring during the formation of the solid (from a liquid), as well as the surface energy of the nucleus. A stable nucleus (of a critical radius r^*) needs to be formed so that it can grow into a larger stable particle. Let us refer to particles of radii smaller than r^* as embryos; the energy for such an embryo formation (ΔG_r) is given by:

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \quad (4.9)$$

where r is the radius of the embryo, ΔG_v is the free energy change per unit volume between the liquid and solid, and γ_{SL} is the interfacial free energy of the liquid and solid.

Below the melting temperature (T_m) of the solid, ΔG_v is negative, whereas the surface free energy, or surface tension γ_{SL} is positive. The two energies compete with each other with increasing value of the embryo radius r . The nature of the resulting curve for ΔG_r is illustrated schematically in Fig. 4.15.

Differentiating Eq. (4.9) with respect to r and equating it to zero at $r = r^*$, we obtain:

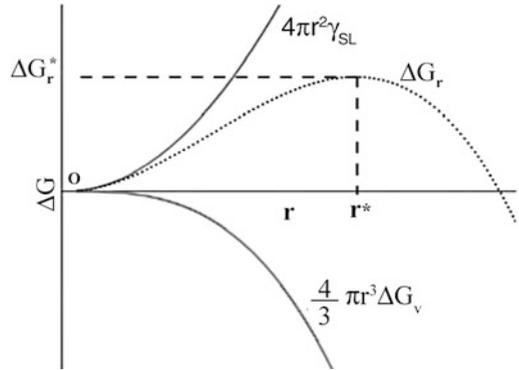
$$4\pi r^{*2} \Delta G_v + 4\pi (2r^*) \gamma_{SL} = 0 \quad (4.10)$$

Hence,

$$r^* = \frac{-2\gamma_{SL}}{\Delta G_v} \quad (4.11)$$

After the critical size r^* , the free energy starts decreasing and the growth begins.

Fig. 4.15 Nucleation process



The energy ΔG_v depends on latent heat of fusion and the degree of undercooling. Undercooling is a result of faster cooling rate than required for the equilibrium cooling. Some finite time is required in any system so that atoms/molecules adjust themselves and acquire the position of minimum energy. The undercooling temperature is given as:

$$\Delta T = T - T_m \tag{4.12}$$

where T_m is equilibrium melting temperature, T – bulk temperature, and ΔH_f is the heat of fusion per unit volume.

It can be shown that

$$\Delta G_v = \frac{\Delta H_f \Delta H}{T_m} \tag{4.13}$$

Therefore,

$$r^* = \frac{-2\gamma_{SL} T_m}{\Delta H_f \Delta H} \tag{4.14}$$

If ΔG_v is the total free energy of the nucleus of radius r , number of clusters n_r can be obtained using

$$n_r = N e^{\left(\frac{-\Delta G_v}{kT}\right)} \tag{4.15}$$

where N is the total number of atoms and k is Boltzmann constant.

In case there is strain caused in the nucleus formation, additional term $\frac{4}{3}\pi r^3 \epsilon$ can be added to the Eq. (4.9). Here ϵ is the strain energy and is positive.

When the nucleation occurs on some foreign particle or surface (e.g. of the container wall or substrate), heterogeneous nucleation is said to occur. This lowers the energy necessary for the nucleation of a particle. Consequently the critical size

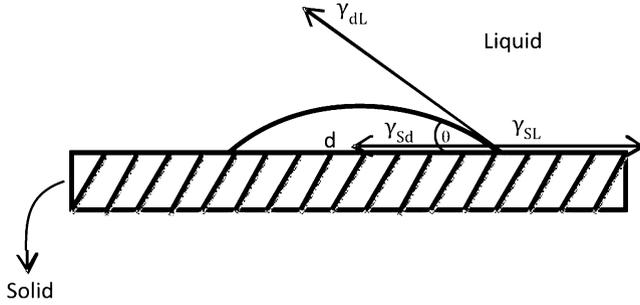


Fig. 4.16 Nucleation on a solid surface

or radius r^* for nucleation is smaller in heterogeneous nucleation than that for homogeneous nucleation. This can be understood as follows.

Consider a solid substrate on which a drop of liquid forms as illustrated in Fig 4.16. γ_{sd} , γ_{sl} and γ_{dl} are the interfacial surface tensions between substrate and liquid drop, surface and liquid and the drop and liquid respectively. It can be seen from Fig. 4.16 that:

$$\gamma_{dl} \cos \theta = \gamma_{sl} - \gamma_{sd} \quad (4.16)$$

Therefore,

$$\Delta G = V\Delta G_v + A_{dl}\gamma_{dl} - \pi r^2\gamma_{dl} \cos \theta \quad (4.17)$$

where V is the volume of the liquid drop; it may be noted that there is change in the volume free energy ΔG_v as discussed with reference to homogeneous nucleation. Hence the critical radius r^* which is given as

$$r^* = \frac{-2\gamma_{dl}}{\Delta G_v} \quad (4.18)$$

also changes. In general, once the nuclei with critical radii r^* are generated, stable nuclei and particle growth starts by addition of atoms or molecules from the solute.

4.4 Synthesis of Metal Nanoparticles by Colloidal Route

Colloidal metal nanoparticles are often synthesized by reduction of some metal salt or acid. For example highly stable gold particles can be obtained by reducing chloroauric acid (HAuCl_4) with tri sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$). The reaction takes place as follows (Fig. 4.17):



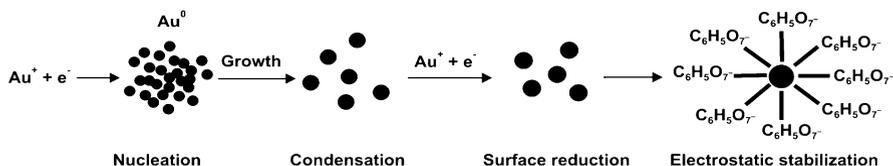


Fig. 4.17 Stabilization by electrochemical double layer formation

The reaction can be carried out in water using the set up shown in Fig. 4.13.

Metal gold nanoparticles exhibit intense red, magenta and other colours, depending upon the particle size. The size dependent optical properties of metal nanoparticles are discussed in Chap. 8. Gold nanoparticles discussed above are stabilized by repulsive Coulombic interactions. It is also possible to stabilize gold nanoparticles using thiol or some other capping molecules.

In a similar manner, silver, palladium, copper and other metal nanoparticles can be synthesized using appropriate precursors, temperature, pH, duration of synthesis etc. Particle size, size distribution and shape strongly depend on the reaction parameters and can be controlled to achieve desired results. It is also possible to synthesize alloy nanoparticles using appropriate precursors.

4.5 Synthesis of Semiconductor Nanoparticles by Colloidal Route

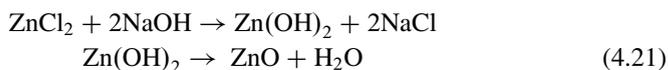
Compound semiconductor nanoparticles can be synthesized by wet chemical route using appropriate salts. Here we shall discuss some methods to obtain semiconductor nanoparticles.

Sulphide semiconductors like CdS and ZnS can be synthesized as nano-particles simply by coprecipitation. For example, to obtain ZnS nanoparticles any zinc salt like zinc sulphate ($ZnSO_4$), zinc chloride ($ZnCl_2$), zinc nitrate ($ZnNO_3$) or zinc acetate ($Zn[CH_3COO]_2$) can be dissolved in aqueous medium and Na_2S is added to the solution. (One can even dissolve H_2S gas in the Zn salt solution).

Following simple reaction



results to give solid colloidal particles of ZnS. To obtain zinc oxide particles one can use NaOH. Following reaction takes place.



Selenide particles can be obtained using appropriate selenium giving salt.

However all these nanoparticles need to be surface passivated as colloids formed in liquids have a tendency to coagulate or ripen due to attractive forces existing between them. The electrostatic and other repulsive forces may not be sufficient to keep them apart. However, as it was also discussed earlier, steric hindrance can be created by appropriately coating the particles to keep them apart. This is often known as ‘chemical capping’ and has become a widely used method in the synthesis of nanoparticles. Advantage with this chemical route is that, one can get stable particles of variety of materials not only in the solution, but even after drying off the liquid. One can even make thin films of the capped particles by spin coating or dip coating techniques. The coating, however, has to be stable and non-interactive with the particle itself except at the surface. Coatings may be a part of post-treatment or a part of the synthesis reaction to obtain nanoparticles. If it is a part of the synthesis reaction, the concentration of capping molecules can be used in two ways i.e. to control the size as well as to protect the particles from coagulation.

Chemical capping can be carried out at high or low temperature depending on the reactants. In high temperature reactions, cold organometallic reactants are injected in some solvent like trioctylphosphineoxide (TOPO) held at a temperature of 300–400 °C. For example when dimethyl cadmium $[\text{Cd}(\text{CH}_3)_2]$ and Se powder were injected in TOPO, CdSe nanoparticles capped with PO_4 groups were obtained. There are, however, other chemicals also which can be used as precursors to obtain high quality particles. It is possible to remove the aliquots at different intervals, as the reaction proceeds, to obtain the particles of different sizes. The particles with high quality and as narrow size distribution as <5 % have been achieved by this method.

Although, this is a very good route of synthesizing the nanoparticles, most of the organo-metallic compounds are prohibitively expensive. Besides they are also toxic and difficult to handle. Such synthesis should, therefore, be carried out only under expert guidance.

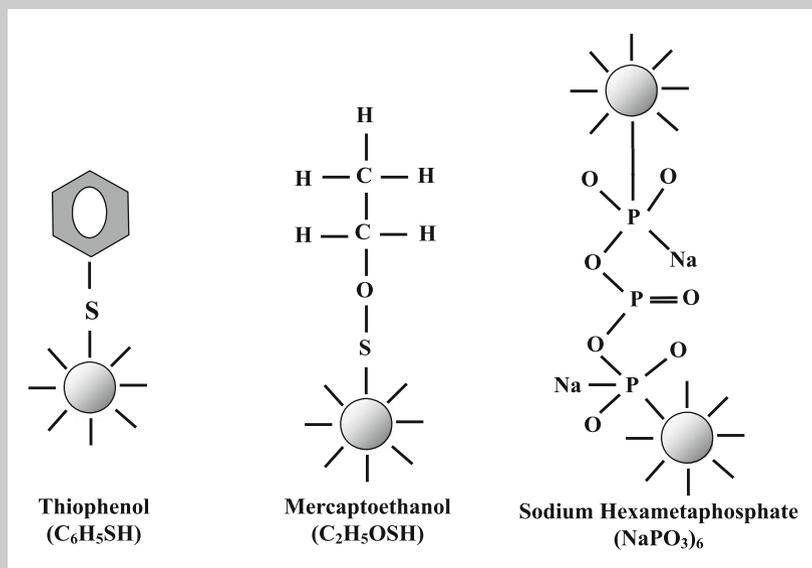
A wide range of metal oxides and other insulators with wide band gap can be synthesized by chemical precipitation method along with suitable surface passivant, if necessary. Some of the oxides and insulators may be stable and may not agglomerate or coalesce easily (Box 4.4).

Box 4.4: Chemical Capping of Nanoparticles

A variety of molecules can be used to cap the nanoparticles. For example capping of metal-sulphide nanoparticles by few organic and inorganic molecules is illustrated in Fig. 4.18.

In another variation of chemical capping method, reactions of inexpensive and non-toxic chemicals like metal chlorides, nitrates, acetates and inorganic salts are performed at moderate temperatures like 80–120 °C. In some cases, it is even possible to synthesize nanoparticles at room temperature. However the initial size distribution can be quite broad. The size distribution

(continued)

Box 4.4 (continued)**Fig. 4.18** Capping of nanoparticles by different molecules

can be narrowed down by a method known as ‘size selective precipitation’. For this one needs to use a proper pair of solvent-nonsolvent liquids. Some of the solvent-nonsolvent pairs are pyridine-hexane, chloroform-methanol or dimethyl sulphoxide-diethyl ether.

The nanoparticles are dispersed in a solvent so as to get an optically clear solution. Nonsolvent solution is then added so that flocculation occurs. Supernatant and flocculate are separated by centrifugation. Precipitate has larger particles and can be separated. Bigger particles, therefore, are first separated from smaller particles and again dispersed in the solvent solution. The process is continued until no change in the size distribution is observed by repeating the procedure.

Advantage of chemical capping method is mainly that nanoparticles are chemically stable over a long time. The thermal stability depends upon the capping molecules used. In most cases, where organic molecules are used, particles are stable upto about 200–250 °C and may find considerable range of applications. Another advantage with both the methods is that while synthesizing the nanoparticles, they can be doped with some metal ions so as to get fluorescent particles at relatively low temperatures. A wide range of semiconductor nanoparticles can be synthesized by this way and are found to be useful in many applications.

4.6 Langmuir-Blodgett (LB) Method

This technique to transfer organic overlayers at air-liquid interface onto solid substrates is known for nearly 70 years. The technique was developed by two scientists Langmuir and Blodgett and bears their names.

In this technique, one uses amphiphilic long chain molecules like that in fatty acids. An amphiphilic molecule (see Fig. 4.19) has a hydrophilic group (water loving) at one end and a hydrophobic group (water hating) at the other end. As an example consider the molecule of arachidic acid, which has a chemical formula $[\text{CH}_3(\text{CH}_2)_{16}\text{COOH}]$. There are many such long organic chains with general chemical formula $[\text{CH}_3(\text{CH}_2)_n\text{COOH}]$, where n is a positive integer. In this case $-\text{CH}_3$ is hydrophobic and $-\text{COOH}$ is hydrophilic in nature.

Usually molecules with $n > 14$ are candidates to form L-B films. This is necessary in order to keep hydrophobic and hydrophilic ends well separated from each other. Figure 4.20 illustrates few examples of different types of molecules which have successfully been used in L-B film deposition.

When such molecules are put in water, the molecules spread themselves on surface of water in such a way that their hydrophilic ends, often called as ‘heads’ are immersed in water, whereas the hydrophobic ends called as ‘tails’ remain in air. They are also surface active agents or surfactants. Surfactants are amphiphilic molecules that is an organic chain molecule in which at one end there is a polar, hydrophilic (water loving) and at the other a nonpolar, hydrophobic (water hating) group of atoms.

Using a movable barrier, it is possible to compress these molecules to come closer together to form a ‘monolayer’ and align the tails. It is, however, necessary that

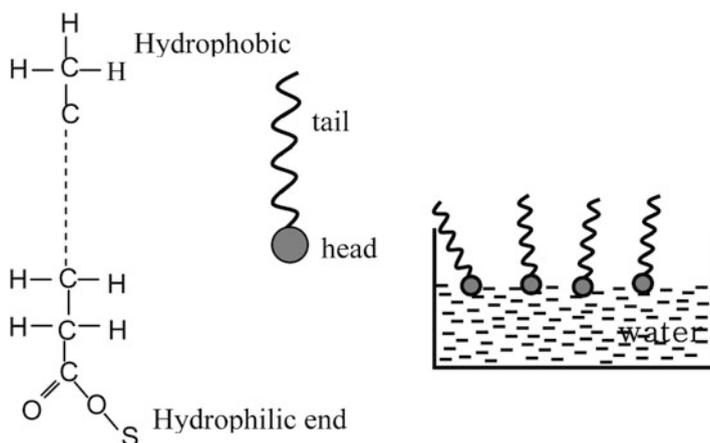


Fig. 4.19 Amphiphilic molecules with hydrophilic and hydrophobic ends to stay with head group immersed in water and tail group in air

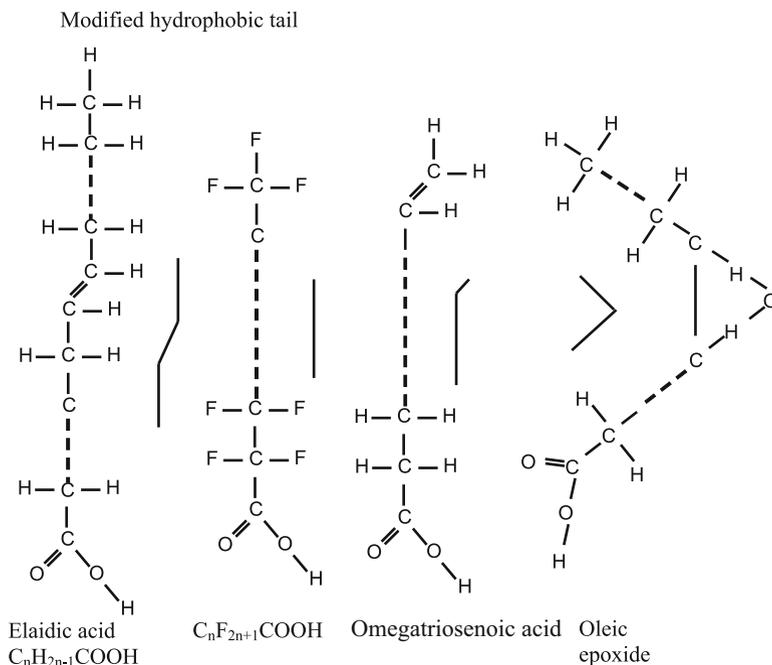


Fig. 4.20 A variety of organic molecules used for L-B thin film deposition

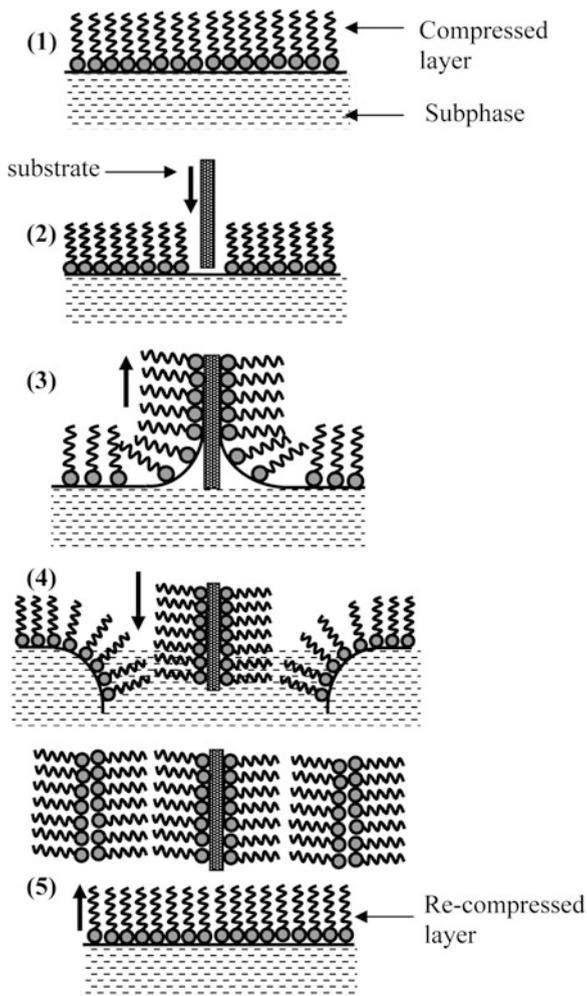
hydrophilic and hydrophobic ends are well separated with $n > 14$. Such monolayers are two dimensionally ordered and can be transferred on some suitable solid substrates like glass, silicon etc. This is done simply by dipping the solid substrate inside the liquid in which ordered organic molecular monolayer is already formed, as shown in Fig. 4.21.

Depending upon the nature of substrate material i.e. whether hydrophobic or hydrophilic, layers are transferred on the solid substrates. A glass slide when dipped in the solution becomes wet with water. Therefore, while it is withdrawn from the liquid the head groups can be easily attached to glass surface. As a result the whole monolayer gets transferred in a manner as if a carpet is pulled. Now the glass substrate has tail groups, which are hydrophobic on outer side.

Therefore as it is dipped in the liquid again, it acquires a second layer with tail-tail coming closer together and while it is pulled back to air, another monolayer of molecules with head-head groups coming together is pulled. The process of dipping-pulling the substrate can be repeated several times to obtain ordered multilayers of molecules. However to keep ordered layers available on water surface, it is necessary to keep constant pressure on the molecules.

In general there are three types of L-B films with different multilayer sequence, as shown in Fig. 4.22, identified. These are known as X, Y and Z type. Y types of films are most commonly found. Although the layers are ordered, there is only the

Fig. 4.21 Deposition of LB films by following steps:
 (1) A monolayer of amphiphilic molecules is formed.
 (2) A substrate is dipped in the liquid.
 (3) The substrate is pulled out, during which ordered molecules get attached to the substrate.
 (4) When the substrate is again dipped, molecules again get deposited as the substrate forming a second layer on the substrate.
 (5) As the substrate is again pulled out, a thin layer gets deposited. By repeating the procedure a large number of ordered layers can be transferred on a substrate



weak Van der Waals interaction between different layers. In this sense even with large number of layers present, the film preserves its two dimensional properties. Lengths of organic molecules as discussed above are typically 2–5 nm. Thus L-B films themselves are good examples of nanostructured materials.

It is also possible to obtain nanoparticles using LB technique. As shown in Fig. 4.23, a metal salt like CdCl_2 or ZnCl_2 is dissolved in water on surface of which a compressed uniform monolayer (single layer of molecules) of surfactant is spread. When H_2S gas is passed in the solution, CdS or ZnS nanoparticles of few tens of nanometers can be formed. Particles are monodispersed (almost one size) in size. If surfactant molecules are not present, uniform nanoparticles are not formed.

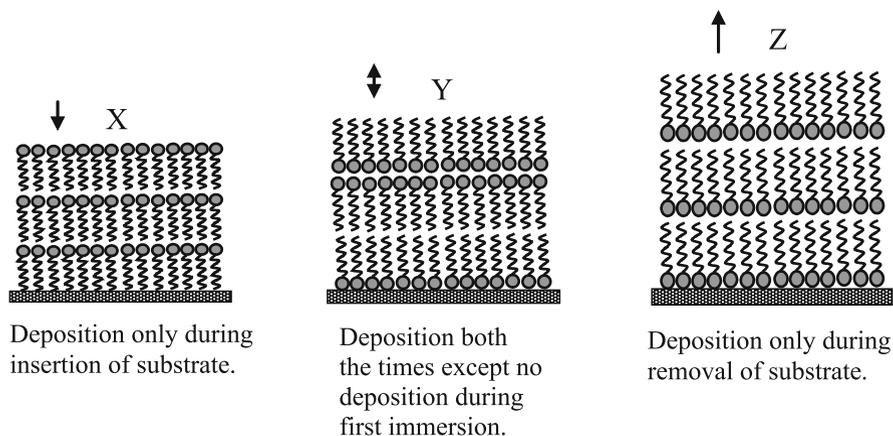


Fig. 4.22 X, Y and Z type L-B films

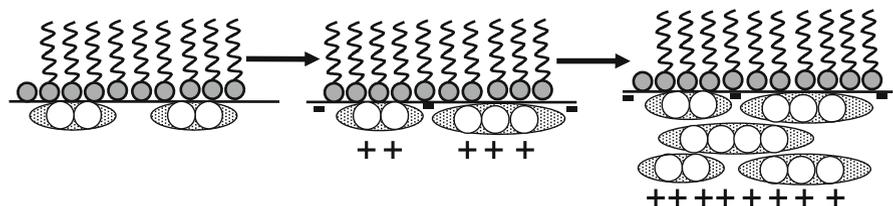


Fig. 4.23 Metal sulphide nanoparticles obtained under the monolayers at water-air interface. The time of hydrogen sulphide treatment increases from top to bottom

4.7 Microemulsions

Synthesis of nanoparticles in the cavities produced in microemulsion is a widely used method. Advantage of this method is the biocompatibility and biodegradability of synthesized materials. Biocompatibility is useful in novel applications like drug delivery of nanomaterials and biodegradability is useful to avoid environmental pollution.

Whenever two immiscible liquids are mechanically agitated or stirred together, they are known to form an ‘emulsion’. The tendency of the liquids is such that the liquid in smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the rest of the liquid in large quantity (for example droplets of fat in milk). The droplet sizes in emulsions are usually larger than 100 nm upto even few millimetres. Emulsions are usually turbid in appearance.

On the other hand there is another class of immiscible liquids, known as microemulsions which are transparent and the droplets are in the range of ~1–100 nm. This is the size needed for the synthesis of nanomaterials (Boxes 4.5 and 4.6).

Box 4.5: Amphiphilic Molecules in Liquids

If amphiphilic molecules are spread in an aqueous solution, they try to stay at air-solution interface with hydrophobic groups in air and hydrophilic groups in the solution (see Fig. 4.24a). Such molecules are known as surfactants (surface active agents). This is similar to what was discussed in L-B film synthesis.

Consider now a situation in which a hydrocarbon molecule solution is put in an aqueous medium. As shown in Fig. 4.24b, the hydrocarbon solution itself would be separated from aqueous solution and float on it. When surfactant molecules are mixed in large quantity in aqueous solution, they would try to form what are known as 'micelles' and 'inverse-micelles' when aqueous solution is mixed in oil. In micelles, the head groups float in water and tails are inside, whereas tails point outwards in case of inverse micelles.

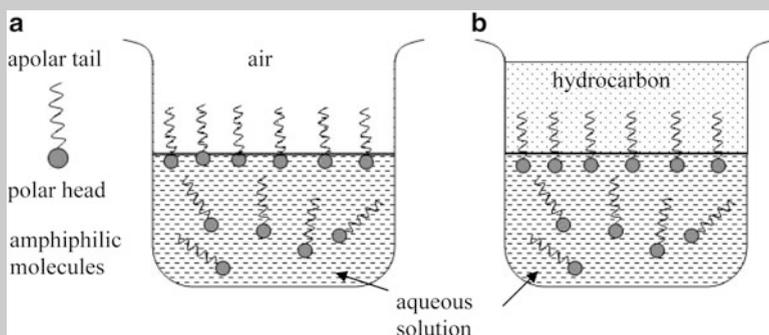
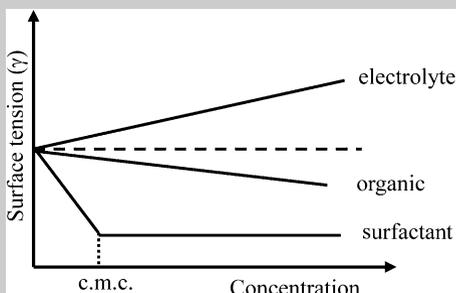


Fig. 4.24 Amphiphilic molecules in aqueous solutions

Box 4.6: Surface Tension of Liquids

Surface tension of a liquid can change if some electrolyte, organic or surfactant solutes are added. General behaviour is shown in Fig. 4.25.

Fig. 4.25 For surfactant molecules γ decreases rapidly upto certain concentration known as critical micelle concentration (c.m.c.)



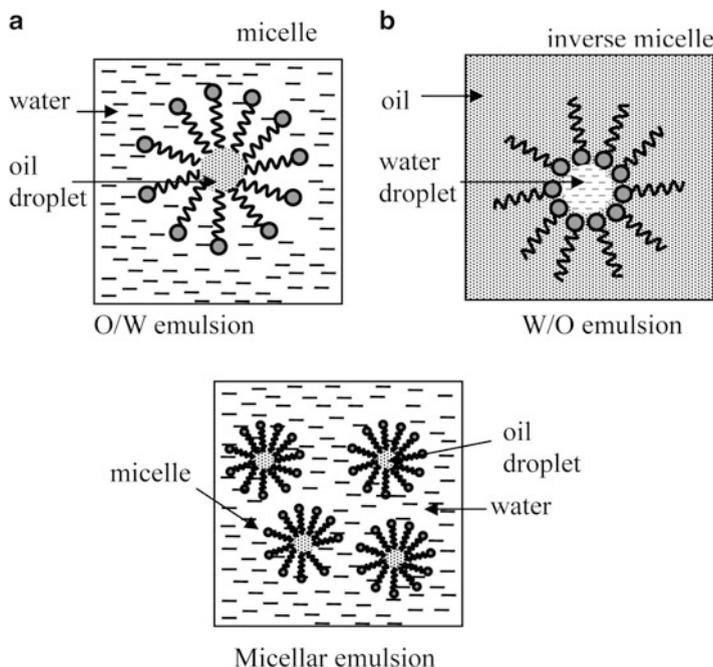
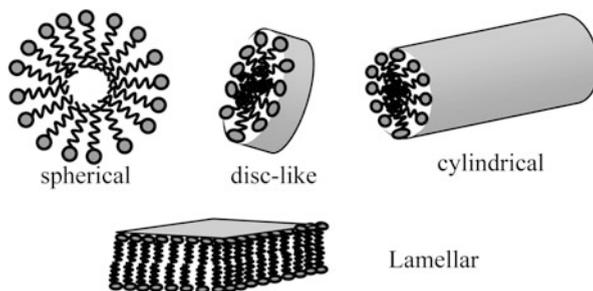


Fig. 4.26 Formation of micelles and inverse micelles

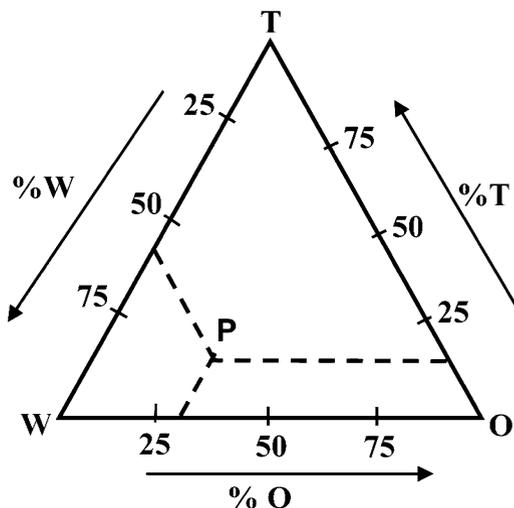
Fig. 4.27 Different shapes of micelles



Microemulsions are stabilized using surfactants (surface stabilized active agents). When an organic liquid or oil (O), water (W) and surfactant (T) are mixed together, under some critical concentration, ‘micelles’ or ‘inverse micelles’ are formed, depending upon the concentrations of water and organic liquid. As shown in Fig. 4.26, micelles are formed with excess water and inverse micelles are formed in excess of organic liquid or oil.

As shown in Fig. 4.26, micelles have the head groups floating in water, whereas tails and tail group filling the cavity along with organic liquid inside. Reverse is the case for inverse micelles. They can be formed in various shapes as well. In Fig. 4.27 different shapes taken by micelles under different synthesis conditions are illustrated.

Fig. 4.28 Ternary phase diagram of water (*W*), oil (*O*) and surfactant (*T*) mixture



The ratio of water (*W*), oil (*O*) and surfactant (*T*) is important to decide which type of micelle will be formed and can be represented in a ternary phase diagram, using a triangle as shown in Fig. 4.28.

Composition can be determined by drawing lines parallel to all three sides of the triangle as shown in Fig. 4.28. Here point *P* denotes 60 % water, 26 % oil and 14 % surfactant.

A modified phase diagram known as ‘Winsor Diagram’ (see Fig. 4.29a) further denotes the types of phases formed.

There is also another type of phase diagram which shows further details as illustrated in Fig. 4.29b.

The critical micelle concentration (CMC) depends upon all *W*, *O* and *T* concentrations as is evident from above diagram. The effect of *T* is to reduce the surface tension of water dramatically below CMC and remain constant above it, as the organic solvent concentration keeps on increasing. Organic solutes also reduce the surface tension to some small extent. If there are any electrolytes used, they slightly increase the surface tension.

There are four types of surfactants in general:

1. Cationic – For example CTAB, $C_{16}H_{33}N(CH_3)_3^+Br^-$
2. Anionic – For example sulphonated compounds with general formula $R-SO_3^-Na^+$
where *R* is C_nH_{2n+1} .
3. Nonionic – For example $R-(CH_2-CH_2-O)_{20}-H$
4. Amphoteric – Some properties are similar to ionic and some to nonionic surfactants as in betaines.

A large number of nanoparticles (metals, semiconductors and insulators) of cobalt, copper, $CaCO_3$, $BaSO_4$, CdS or ZnS have been synthesized using

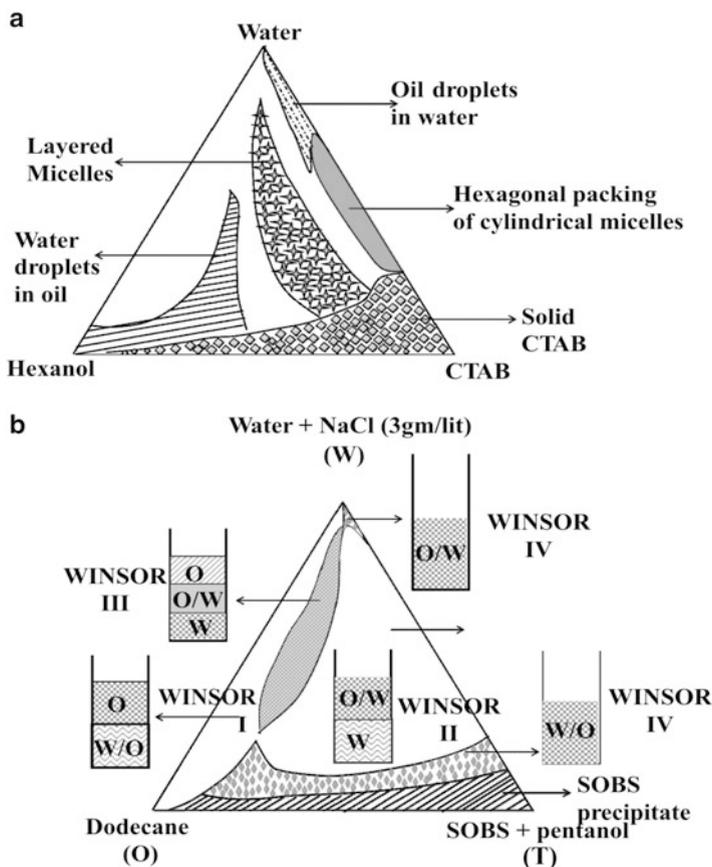


Fig. 4.29 Winsor phase diagram with different phases (a) water-hexanol-centryltrimethylammoniumbromide (CTAB) and (b) water and NaCl-dodecane-paraocetylbenzene sodium sulphate (SOBS) and pentanol

microemulsions or inverse micelles. As an example, consider the synthesis of cobalt nanoparticles. A reverse micelle solution of water and oil can be stabilized using a monolayer of surfactant like sodium bis (2-ethylhexyl)sulfosuccinate or Na(AOT). The droplet diameter is controlled simply by controlling the amount of water. Two micelle solutions having same diameter of droplets can be formed. Thus one solution should have Co(AOT)_2 i.e. cobalt bis(2-ethylhexyl)sulfosuccinate and the other should have sodium tetrahydroborate (NaBH_4 i.e. sodium borohydride). When two solutions are mixed together the resultant solution appears clear but the colour changes from pink to black. One can find by electron microscopy or some other analysis that cobalt nanoparticles are formed.

4.8 Sol-Gel Method

As the name suggests sol gel involves two types of materials or components, 'sol' and 'gel'. Sol gels are known since the time when M. Ebelman synthesized them in 1845. However it is only since the last one or two decades that considerable interest in it, both in scientific and industrial field, has generated due to realization of the several advantages one gets as compared to some other techniques. First of all sol gel formation is usually a low temperature process. This means less energy consumption and less pollution too. It is therefore not surprising that in the nuclear fuel synthesis it is a desired process. Although sol-gel process generates highly pure, well controlled ceramics it competes with other processes like CVD or metallo-organic vapours derived ceramics. The choice of course depends upon the product of interest, its size, instrumentation available and ease of processing. In some cases sol-gel can be an economical route, provided precursors are not very expensive. Some of the benefits like getting unique materials such as aerogels, zeolites, and ordered porous solids by organic-inorganic hybridization are unique to sol-gel process. It is also possible to synthesize nanoparticles, nanorods or nanotubes using sol-gel technique.

Sols are solid particles in a liquid (see Fig. 4.30). They are thus a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid). A sol gel process involves formation of 'sols' in a liquid and then connecting the sol particles (or some subunits capable of forming a porous network) to form a network. By evaporating the liquid, it is possible to obtain powders, thin films or even monolithic solid. Sol gel method is particularly useful to synthesize ceramics or metal oxides although sulphides, borides and nitrides also are possible.

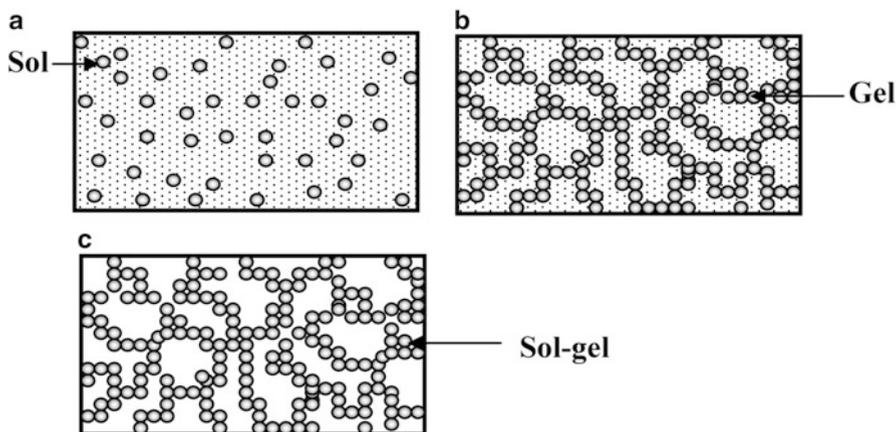


Fig. 4.30 Sol (a), gel (b) and sol-gel (c) monolithic solid

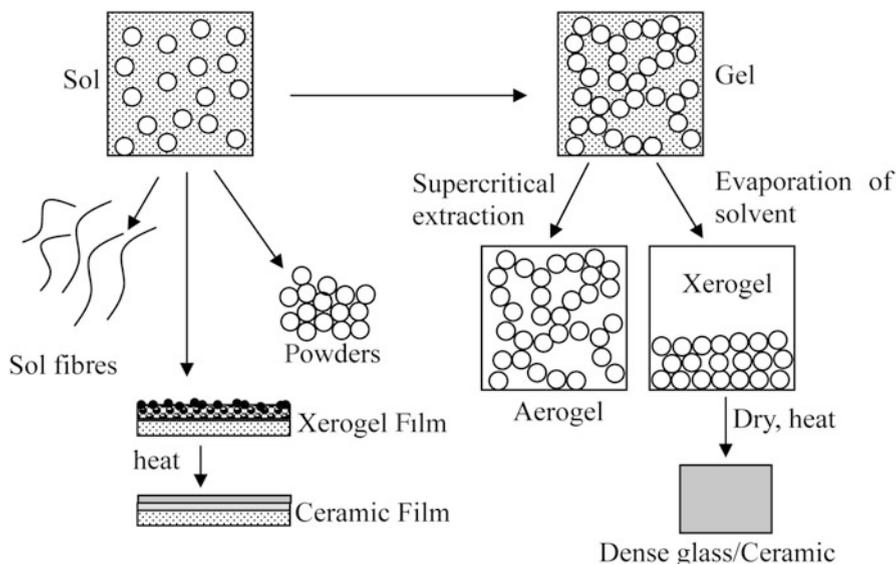


Fig. 4.31 Sol-gel options

Synthesis of sol-gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes as shown in Fig. 4.31. Precursors (starting chemicals) are to be chosen so that they have a tendency to form gels. Both alkoxides or metal salts can be used. Alkoxides have a general formula $M(\text{ROH})_n$, where M is a cation and R is an alcohol group, n is the number of (ROH) groups with each cation. For example (ROH) can be methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$) etc. bonded to a cation like Al or Si . Salts are denoted as MX , in which M is a cation and X is an anion like in CdCl_2 , Cd^+ is a cation and Cl^- is an anion.

Although it is not mandatory that only oxides be formed by a sol-gel process, often oxide ceramics are best synthesized by a sol-gel route. For example in silica, SiO_4 group with Si at the centre and four oxygen atoms at the apexes of tetrahedron are very ideal for forming sols with interconnectivity through the corners of tetrahedrons, creating some cavities or pores (See Fig. 3.4 in Chap. 3).

Due to its higher electronegativity as compared to metal cations, Si is less susceptible to nucleophilic attacks.

By polycondensation process (i.e. many hydrolyzed units coming together by removal of some atoms from small molecules like OH), sols are nucleated and ultimately sol-gel is formed.

We shall discuss two special types of sol-gel materials viz. zeolites and aerogels in Chap. 11. We shall also see that there are recent methods to combine microemulsion method with sol-gel method to produce some novel materials.

4.9 Hydrothermal Synthesis

This synthesis method is useful to make a large scale production of nano to micro size particles. In this technique adequate chemical precursors are dissolved in water and placed in vessel made of steel or any other suitable metal which can withstand high temperature typically upto 300 °C and high pressure above 100 bars. The vessel, known as *autoclave*, is usually provided with temperature and pressure control as well as measuring gauges as illustrated in Fig. 4.32.

It is a very old technique, probably first used by the German scientist Robert Bunsen, way back in 1839 to synthesize crystals of strontium and barium carbonates. He used a thick glass tube and used temperature above 200 °C and pressure more than 100 bars. The technique was later used mostly by geologists and has become popular amongst nanotechnologists due to the advantages like large yield and novel shapes and sizes that can be obtained using this technique.

The technique becomes useful when it is difficult to dissolve the precursors at low temperatures or room temperature. It is also advantageous to use the technique to grow nanoparticles if the material has a high vapour pressure near its melting point or crystalline phases are not stable at melting point. The uniformity of shapes and sizes of the nanoparticles also can be achieved by this technique. Various oxide, sulphide, carbonate and tungstate nanoparticles have been synthesized by the hydrothermal synthesis.

Another variation of hydrothermal synthesis technique is known as *forced hydrolysis*. In this case usually dilute solutions (10^{-2} to 10^{-4} M) of inorganic metal salts are used and hydrolysis is carried out at rather higher temperatures than 150 °C.

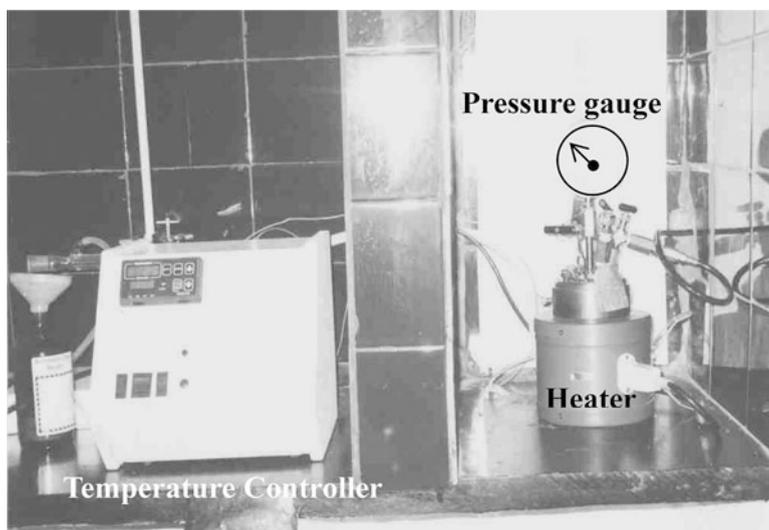


Fig. 4.32 Photograph of an autoclave set up

4.10 Sonochemical Synthesis

In this technique the reactivity of the precursors is enhanced by taking the advantage that large amount of energy can be released when bubbles burst in a liquid. Bubbles are formed (see Fig. 4.33) by using ultrasonic waves in a frequency range of ~ 20 kHz–2 MHz. It can be considered as an alternative method to enhance the chemical reactions in liquids by heating and/or pressurizing.

Although it is not well understood yet as to how nanoparticles can be synthesized using sonochemical method, it is well agreed upon that creation, growth and collapse of bubbles in liquids is most important pathway of causing the reactions. The ultrasonic waves while passing through the liquids create very small bubbles which keep on growing until they reach a critical size and then burst, releasing very high energy to locally reach a temperature of $\sim 5,000$ °C and a pressure of few hundred times that of atmospheric pressure. For the reaction to occur in the gas phase the solute in the liquid should diffuse to the growing bubble. The reaction can also occur in the liquid phase at exploding bubble where in the interfacial region surrounding the bubble (~ 200 nm distance) the temperature as high as $\sim 1,600$ °C can be reached. Typically the size of a bubble can be from ten to few tens of microns. Careful use of the solvents and solutes are very important. Non-volatile liquids would prevent formation of bubbles, which is desired, as only reactants should find their place inside the bubble in the form of vapour. Solvents should be inert and stable to ultrasonic irradiation. Interestingly, the cooling rates also can be as high as 10^{11} °C or more. Such a high cooling rate gives rise to amorphous nanoparticles as the atoms do not have sufficient time to reorganize. However amorphous particles can be more active than the crystalline particles of the same size and same material. This can be useful in some fields like catalysis. Various nanoparticles like ZnS, CeO₂ and WO₃ have been synthesized using sonochemical method.

The bubbles after their initiation, grow as shown in the schematic diagram (Fig. 4.33). Bubbles expand progressively in the region of rarefaction and contract

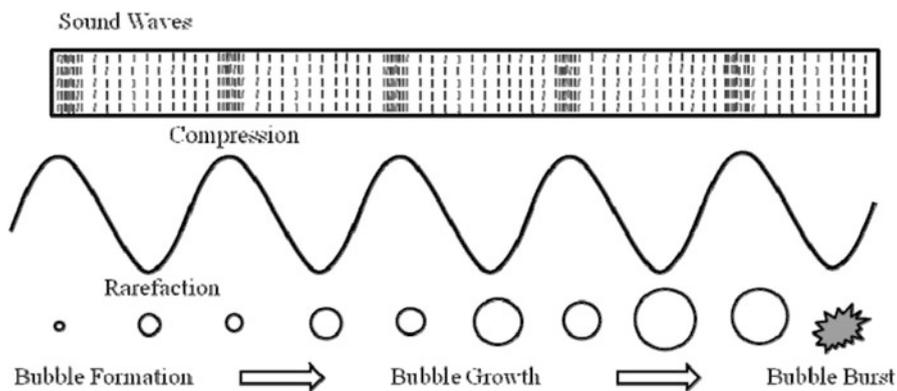


Fig. 4.33 Ultra-sound waves form compressions and rarefactions, shown as a sine wave

at compressions but quickly attain a micrometre size and ultimately burst releasing huge energy. Temperature rises to $\sim 5,000$ °C and pressure is more than 100 times atmospheric pressure.

4.11 Microwave Synthesis

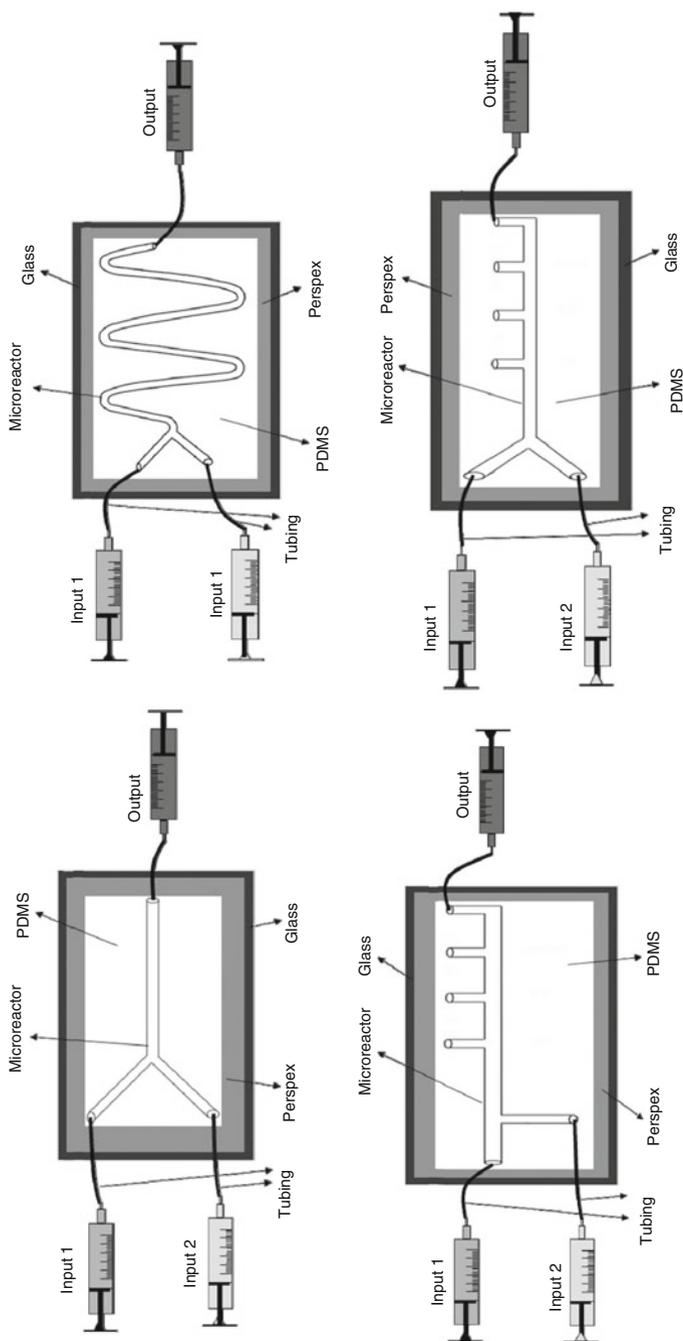
Use of microwave ovens for heating or cooking food is very common. Its entry in the scientific laboratories took place around 1986 when it was demonstrated by some scientists that rapid, large scale and uniform synthesis of materials is possible even using a domestic microwave oven. Kitchen microwave ovens, however, are not any more considered for the controlled chemical synthesis as there is no good control on stirring, temperature or power which is necessary for scientific equipment. However, due to its several advantages microwave synthesis has been used in research laboratories with equipment capable of controlling various parameters.

Microwaves are a part of electromagnetic spectrum with very long wavelength and frequencies in the range of ~ 300 – $300,000$ MHz. However, only certain frequencies are reserved for domestic and other equipment, rest being used for communication purposes. A microwave has oscillating electric and magnetic fields associated with it which produces nodes and antinodes and correspondingly hot and cold spots in a vessel. This would lead to non-uniformities. Therefore sometimes only a 'single mode' is used in which length of the cavity (or reaction vessel) is equal to a single wave only. In a microwave apparatus heating is caused only due to a process in which molecules in a solution try to orient their dipoles appropriately to align themselves in the direction of the electric field. In the process they too oscillate, generating heat in the medium. Advantage in this case is that the external energy is not wasted in heating of the vessel.

Several types of oxide, sulphide and other nanoparticles have been synthesized to obtain various shapes and sizes. The reaction time is greatly reduced and the products are uniform in size and shape.

4.12 Synthesis Using Micro-reactor or Lab-On-Chip

Micro-reactor or lab-on-chip is a relatively new method of synthesizing nanoparticles in small quantities. Basically, very narrow channels (less than about 100 μm upto few tens of nm in width and depth) are made in some suitable substrates like glass, silicon or polymers like poly-dimethylsiloxane (PDMS) using lithography techniques. Similar to an electronic circuit in a semiconductor chip, these channels make some circuit where the fluids can mix. There can be some mixer regions where stirring takes place with the help of magnetic or some other actuation. There can be some valves to control the flow of liquids. The channels can be of short or long length depending upon the requirements and are designed to suit a particular

**Fig. 4.34** Schematic of microreactor set up

requirement. The size of the whole reactor can be as small as $\sim 10 \text{ cm}^2$. The liquids may be aqueous or non-aqueous and suitable reactor will have to be chosen according to the reactions to be carried out. It is also possible to heat some of the reactors to enhance the rates of reaction. The liquids should not react with the reactor material or percolate inside its body. The liquids are injected inside the channels using syringe pumps. Figure 4.34 illustrates few simple designs of a microreactor set up without complicated valves, mixers and other components.

Advantage of synthesizing nanomaterials in microreactors is that reactions can be carried out in a very short time using small amounts of reactants. This is advantageous when expensive or toxic reactants are to be used. Due to small amounts involved, the risk of pollution is minimized. Short synthesis time enables many reactions to be carried out in a short time. Therefore, optimization of reaction parameters can be done very quickly. However, due to small channel size, the fluid flow in channels and in large glass flask reactor may differ. However, using parallel processing one can increase the quantity of the product to be obtained in microreactors. One, however, has to be careful that if the particles grow to large size they may clog the channels. Cleaning of the channels also can pose problems. However disposable polymer-based inexpensive microreactors can be a good solution to avoid the cross contaminations.

There are many reports now which show that TiO_2 , ZnS, CdSe, Au, Ag etc. nanoparticles with narrow size distribution have been achieved using microreactors. Moreover doping of nanoparticles also is possible in microreactors. In short, whatever the synthesis is carried out in a chemistry laboratory can be carried out in the lab-on-chip.

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